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CALCULATION OF THE IN-PLANE FORCE CONSTANTS AND VIBRATIONAL SPECTRA OF PYRIDINE AND ITS DEUTERATED DERIVATIVES BY THE CNDO/2 FORCE METHOD

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ABSTRACT

The in-plane vibrations of pyridine and its deuterated derivatives (4-d_1, 2,6-d_2, 3,5-d_2, and d_5) have been studied with the CNDO/2 force method. The calculated values of the force field scaled by five empirical parameters yield good agreement with the experimental spectra. The results seem to permit the reassignment of some bands.

INTRODUCTION

The knowledge of force constants and the prediction of vibrational spectra is of practical importance. If transferable force constants are known the vibrational spectra can be calculated [1]. The force field, determined from the experimental spectra, is unfortunately not transferable in general.

Convenient and transferable force constants reproducing the spectra are known in only a few cases, e.g. for paraffins [2] and for fluorobenzenes [3]. In other cases the great number of unknown parameters and the uncertain assignments render the determination of a consistent force field difficult.

Calculation of the spectra by quantum chemical methods overcomes the above difficulties. Ab initio calculations [4] give good results but their use is restricted to small molecules. For bigger molecules semi-empirical methods are used. The results of Török, Pulay and co-workers [5—9] show that the CNDO/2 parametrization procedure allows good agreement with the experimental spectra. The use of this method is especially important in the determination of pure deformational and deformational—stretching coupling force constants. The calculated absolute values of the force constants are higher than the real ones but their relative magnitudes are correct. After being scaled by empirical factors satisfactory force constants are obtained. For force constants corresponding to different types of internal coordinates different scaling factors are used.

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The objective of the present work was, apart from confirming the correctness of the method, to obtain a useful force field for pyridine and to check the foregoing assignments.

METHOD

In the force method [5, 10] the energy is calculated for distorted forms of the equilibrium position. The first derivatives, the forces on the atoms in these distorted configurations are calculated analytically while the force constants are then obtained by simple numerical derivation of the forces.

Using CNDO/2 wave functions no numerical instabilities appear if the distortion of the internal coordinates does not exceed 0.02—0.03 Å or radian [9]. In the present study the change of the coordinates was unanimously 0.02 Å or radian in positive and negative directions from the equilibrium position. A separate calculation was done for both directions to test the effect of anharmonicity.

On the basis of the calculations of Kozmutza and Pulay [6] and theoretical considerations of Schwendeman [11] it was concluded that experimental geometrical parameters would be more useful for these calculations than calculated ones. Thus, instead of using an energy-minimized geometry calculated by the CNDO/2 procedure, experimental data from a microwave spectrum were taken. The geometrical parameters of the equilibrium position given by Bak et al. [12] figure in Table 1 while the non-regular pyridine hexagon is shown in Fig. 1.

Pyridine and its derivatives considered here all belong to the point group C_{2v}. Among their 19 in-plane normal modes of vibration 10 belong to the A_1 and 9 to the B_1 species. The internal coordinates used are listed in Table 2 and shown in Fig. 1.

TABLE 1

Cartesian coordinates of the atomic nuclei of pyridine (in Å) in the coordinate system of Fig. 1 [12]

	x	y
H_7	2.0557	−1.2761
H_8	2.1526	1.2055
H_9	0.0	2.4924
N_1	0.0	−1.3949
C_2	1.1416	−0.6929
C_3	1.1974	0.7005
C_4	0.0	1.4151

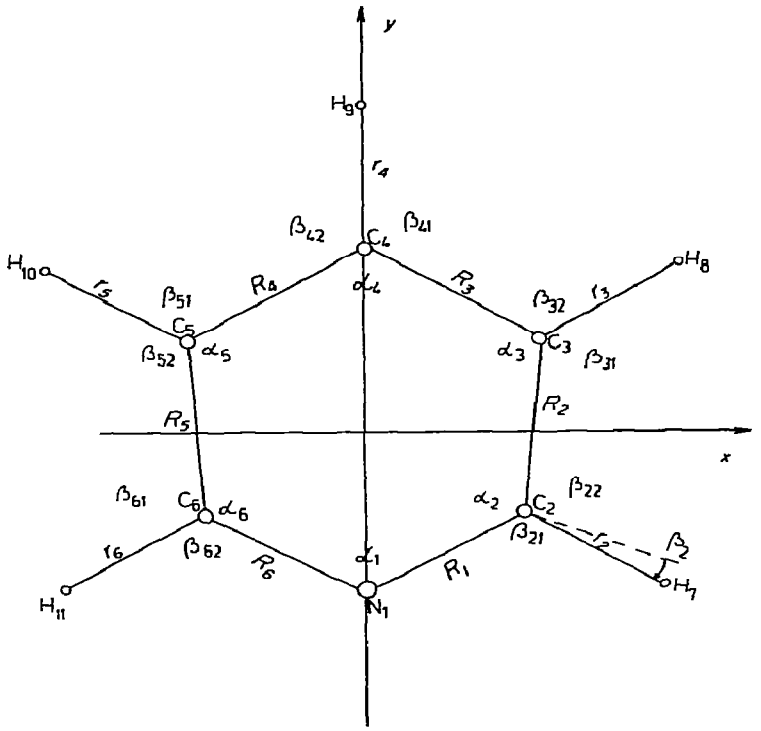

Fig. 1. Position of the atoms and internal coordinates in pyridine (see Tables 1 and 2)

TABLE 2

Internal coordinates

No. of coordinates	Type	Definition of the coordinates	Significance
1, 2, 3, 4, 5, 6	stretching	ΔR_i ($i = 1 \ldots 6$)	change in the length of the C_2—N_1 resp. C_6—N_1 and of the C_i—C_{i-1} ($i \neq 1, 2$) bonds
7, 8, 9, 10, 11	stretching	Δr_i ($i = 2 \ldots 6$)	change in the length of the C_i—H_{i+5} bonds
12, 13, 14, 15, 16	bending	$\beta_i = \beta_{i2} - \beta_{i1}$ ($i = 2 \ldots 6$)	change in the HCC angles
17	bending	$\tilde{\alpha}_1 = \alpha_1 - \alpha_2 + \alpha_3 - \alpha_4 + \alpha_5 - \alpha_6$	change in the CCC angles
18	bending	$\tilde{\alpha}_2 = 2\alpha_1 - \alpha_2 - \alpha_3 + 2\alpha_4 - \alpha_5 - \alpha_6$	change in the CCC angles
19	bending	$\tilde{\alpha}_3 = \alpha_2 - \alpha_3 + \alpha_5 - \alpha_6$	change in the CCC angles

RESULTS AND DISCUSSION

Force field

The method described above served for the calculation of a rough force field for pyridine. As already mentioned, these directly calculated CNDO/2 values must be adjusted using empirical factors to eliminate CNDO-approximation errors.

The scaling procedure has already been described [5—9]: the empirical factors in question are related to the different types of coordinates. The choice of coordinates is governed by theoretical considerations, those of Table 2 being set up in accordance with ref. 13. In the present case there are five factors which correspond, respectively, to CH stretching, CC stretching, CN stretching, CCH bending and CCC bending coordinates. The scaling factor c_i corresponding to a given type of coordinate is obtained by dividing by the calculated value that experimental F_{ii} element which seems to be the most reliable for the given coordinate. Then, all the calculated diagonal force

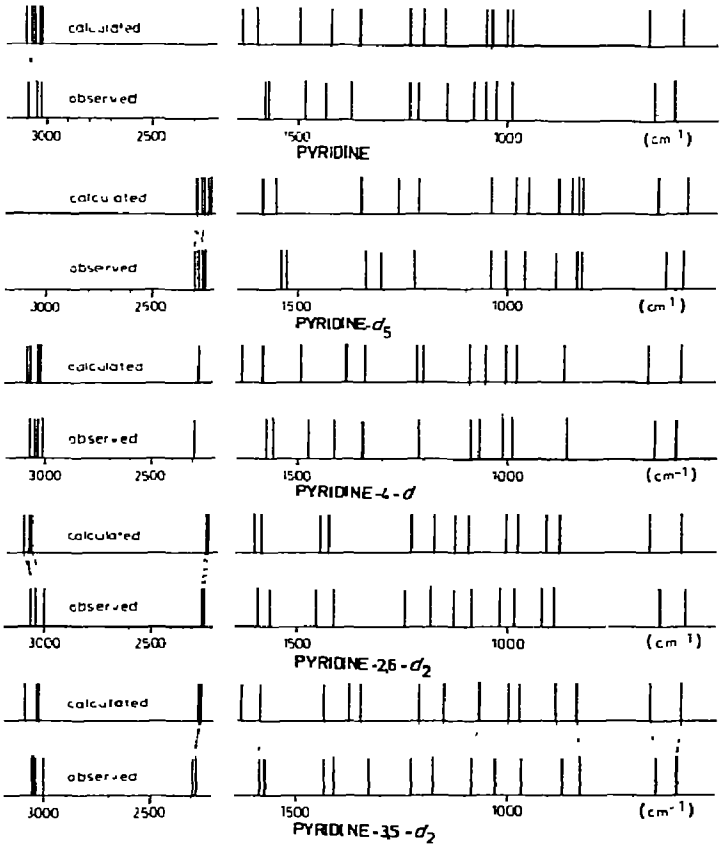

Fig. 2. Bar-diagram of the calculated and observed frequencies of pyridine and its deuterated derivatives (see Tables 3 and 5); dotted lines show correspondence.

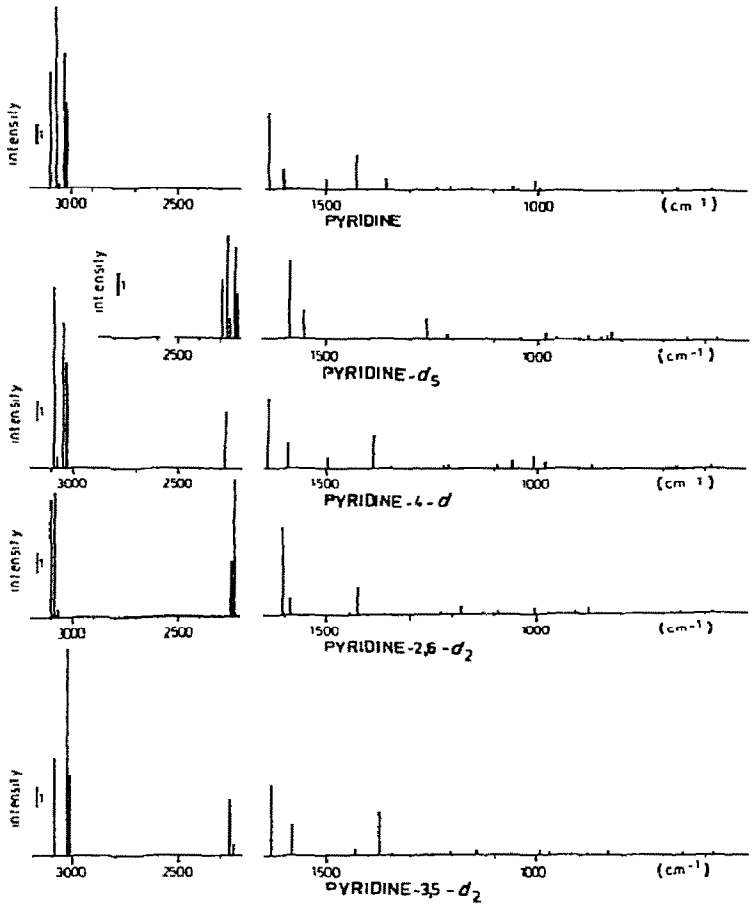

Fig. 3. Diagram of calculated intensities.

constants, including other symmetry species, are multiplied by the same factor (c_i). The same procedure is repeated for the remaining four types of coordinates. The off-diagonal F_{ij} are corrected by $(c_i c_j)^{\frac{1}{2}}$. Thus, the diagonal constants are experiment values while corrected theoretical values appear as off-diagonal constants in the force field.

Before evaluating the correcting factors for pyridine we checked whether the factors already known for benzene and its derivatives [9] could be applied. The similarity of the pyridine and benzene molecules, arising from the isoelectronicity of nitrogen and the CH group of benzene, has often been used in normal coordinate calculations (e.g., [14]). However, while in previous papers the force constants of benzene were applied for pyridine, in the present work a separate CNDO/2 calculation of the force field for pyridine was done. Only the known scaling factors of benzene [9] were employed: $c(\mathrm{CH}) = c(\mathrm{CC}) = 0.382$; $c(\mathrm{CCH}) = 0.787$; $c(\mathrm{CCC}) = 1.19$. Unfortunately, the influence of the nitrogen atom is rather important, the deviation of the frequencies calculated in this way being large enough (see Table 3) to necessitate the use of other correcting factors.

TABLE 3

Experimental and calculated frequencies of pyridine (in cm^{-1}); the originally assigned values appear in parentheses

Symmetry	Notation [19]	Exp. [19]	Calculated with scaling factors of ref. 9	Present calc.	Character of vibration from the CNDO/2 force method
A_1	ν_1	992	1028	993	α(CCC), (ν(CN), ν(CC))
	ν_2	3054	3080	3067	ν(CH)
	ν_{6a}	605	609	588	α(CCC), (resp. α(NCC))
	ν_{8a}	1583	1729	1637	ν(CC)
	ν_{9a}	1218	1224	1203	β(CH)
	ν_{12}	1029	1067	1004	α(CCC), (resp. α(NCC))
	ν_{13}	3054	3096	3092	ν(CH)
	ν_{18a}	1068	1103	1055	β(CH), ν(CN)
	ν_{19a}	1482	1530	1499	β(CH), ν(CN)
	ν_{20a}	3036	3071	3037	ν(CH)
B_1	ν_3	1235[a] (1217)	1322	1236	ν(CC), β(CH)
	ν_{6b}	652	691	669	α(CCC)
	ν_{7b}	3036[b] (3054)	3075	3038	ν(CH)
	ν_{8b}	1572	1689	1599	ν(CN), ν(CC)
	ν_{14}	1375	1353	1356	ν(CN), β(CH)
	ν_{15}	1148	1171	1157	β(CH)
	ν_{18b}	1057[a] (1068)	1098	1044	β(CH)
	ν_{19b}	1439	1456	1428	β(CH)
	ν_{20b}	3083	3092	3072	ν(CH)

[a]From ref. 24. [b]From ref. 21.

Introducing a new factor for the CN stretching coordinate and varying the others with a least squares method the following correction factors were obtained: c(CN) = 0.320; c(CC) = 0.344; c(CH) = 0.380; c(CCH) = 0.813 and c(CCC) = 1.14. The experimental spectrum of pyridine and some deuterated derivatives (d_5; 4-d_1; 2, 6-d_2 and 3, 5-d_2) were taken into consideration for the above calculation.

As the error due to the CNDO-approximation is fairly systematic for stretching-type coordinates, it could be expected that the corresponding scaling factors are the same for different molecules. In fact, the value corresponding to the CH stretching coordinate is nearly the same as that employed for various molecules in refs. 6, 8 and 9 but that for the CC stretching is influenced by the skeleton N-atom and undergoes a change of 10%. The error is, however, less systematic for bending coordinates and the variation of the corresponding scaling factors cannot be so easily explained.

It should be realised that this method of calculation is not just a mani-

pulation of numbers: with five empirical parameters the complete force field is well reproduced, which can be seen by comparing the calculated and experimental frequencies (see later). However, many more parameters are needed for normal coordinate calculations.

The scaled F-matrix is represented in Table 4. The original values (resulting directly from the CNDO/2 calculation) are given for the first column and those for the diagonal elements are given in parentheses. The rows refer to the coordinates of Table 2.

Comparing this force field with the normal coordinate calculations for benzene of Duinker and Mills [15], the results of Whiffen [16], or the CNDO/2 calculations of Fogarasi and Pulay [9], the present values seem to be very reasonable. However, the normal coordinate calculations of Long, Murfin and Thomas (LMT) [14], based on Whiffen's force field for benzene [16], show a surprising deviation. In their work, among other neglected factors, they considered the CN and CC bonds to be identical, and hence the values of the corresponding force constants of LMT to be the same. As the difference between the CN and CC bond lengths is at least 0.05 Å, the present distinction, i.e. a larger value for the force constant of the CN stretching, seems to be more realistic. Also, while the other diagonal constants of Table 4 agree fairly well with those of LMT, the interaction constants differ significantly. There are many more non-zero terms in our Table 4: a number of interactions do not appear in [14] because of the neglected factors. On the other hand, in a number of cases the constants are of opposed sign (e.g., for F_{13} we find a negative, LMT a positive value; even for benzene a negative value is suggested for meta-interaction by Scherer and Overend [17]). The present force field, which results from a separate calculation for pyridine, shows that the nitrogen influences the force field compared with benzene more than was expected earlier; pyridine has a more complex force field and some former simplifications are not justified.

Assignments

The primary importance of the present force constants is checking of previous assignments [18—24]. The scaled CNDO/2 force constants and dipole moment derivatives yield the frequencies and i.r. intensities shown in Tables 3, 5 and 6 and in Figs. 2 and 3, respectively.

Our calculations for pyridine support the recent slight modifications, (ν_3 and ν_{18}) of Suzuki and Orville-Thomas [24] and the earlier one (ν_{7b}) of Wilmshurst and Bernstein (WB) [21], in the original assignment of Corrsin, Fax and Lord (CFL) [19], but no other changes in the assignment were necessary (see Table 3).

Good agreement was obtained for pyridine-4-d_1 with the experimental results of Anderson et al. [20] modified with Raman data (ν_2 and ν_{12}) by WB [21] (Table 5).

In the cases of pyridine-2,6-d_2 and 3,5-d_2 the assignment of WB [21] was

TABLE 4

In-plane force constants of pyridine (in mdyn A^{-1}); values in parentheses are directly calculated, non-scaled CNDO-values

Notation	ΔR_1	ΔR_2	ΔR_3	ΔR_4	ΔR_5	ΔR_6	Δr_2	Δr_3
ΔR_1	7.155 (22.337)							
ΔR_2	0.833 (2.512)	6.155 (17.910)						
ΔR_3	−0.405 (−1.222)	0.757	6.208 (18.063)					
ΔR_4	0.452 (1.365)	−0.383	0.763	6.208 (18.063)				
ΔR_5	−0.397 (−1.198)	0.381	−0.383	0.757	6.155 (17.910)			
ΔR_6	0.833 (2.601)	−0.397	0.452	−0.405	0.833	7.155 (22.337)		
Δr_2	0.227 (0.652)	0.181	0.015	−0.026	−0.023	0.014	5.106 (13.459)	
Δr_3	0.016 (0.046)	0.162	0.175	0.013	−0.020	−0.021	0.0	5.201 (13.709)
Δr_4	−0.018 (−0.052)	0.012	0.175	0.175	0.012	−0.018	0.003	0.0
Δr_5	−0.021 (−0.060)	−0.020	0.013	0.175	0.162	0.016	0.001	0.002
Δr_6	0.014 (0.040)	−0.023	−0.026	0.015	0.181	0.227	0.002	0.001
β_2	−0.183 (−0.360)	0.161	0.009	0.002	0.012	−0.006	−0.011	−0.006
β_3	−0.018 (−0.035)	−0.159	0.165	0.007	−0.011	0.008	0.008	−0.001
β_4	0.005 (0.009)	−0.008	−0.161	0.161	0.008	−0.005	−0.005	0.009
β_5	−0.008 (−0.017)	0.011	−0.007	−0.165	0.159	0.018	0.0	−0.005
β_6	0.006 (0.012)	−0.012	−0.002	−0.009	−0.161	0.183	0.005	0.0
$\bar{\alpha}_1$	0.039 (0.064)	−0.017	−0.010	−0.010	−0.017	0.039	0.150	−0.141
$\bar{\alpha}_2$	0.151 (0.251)	−0.101	0.067	0.067	−0.101	0.151	0.078	0.079
$\bar{\alpha}_3$	0.183 (0.304)	−0.018	−0.148	0.148	0.018	−0.183	−0.154	0.131

taken as a basis (Table 5). Two changes are suggested for both of them. For 2,6-d_2 Zerbi et al. [23] propose the very weak 1345 cm^{-1} band (ν_{14} (B_1) of ref. 21), not appearing in the gas phase, as an overtone of two out-of-plane frequencies and suggest the band of 1258 cm^{-1} for ν_{14}. On the basis of Tables 5 and 6, the attribution of the 1243 cm^{-1} band, which also appears in the Raman spectrum, seems to be more justified. Similarly, [23] suggests the band at ~902 cm^{-1} for ν_{18b} (B_1) instead of the 860 cm^{-1} band. Although 902 cm^{-1} is nearest our calculated value of 909 cm^{-1}, the assignment is doubtful since the band at 915 cm^{-1}, which appears in both i.r. liquid and vapor spectra, is equally supported by the present results; the 915 cm^{-1} band is preferred here.

While the present results for pyridine-3,5-d_2 confirm Zerbi's [23] proposition that the ν_3 (B_1) mode should be reassigned and that the band at

Δr_4	Δr_5	Δr_6	β_2	β_3	β_4	β_5	β_6	$\bar{\alpha}_1$	$\bar{\alpha}_2$	$\bar{\alpha}_3$
5.265 (13.879)										
0.0	5.201 (13.709)									
0.003	0.0	5.106 (13.459)								
0.006	0.0	—0.005	0.580 (0.714)							
—0.009	0.005	0.0	0.003	0.516 (0.635)						
0.0	—0.009	0.005	—0.009	0.008	0.525 (0.646)					
0.009	0.001	—0.008	—0.001	—0.009	0.008	0.516 (0.635)				
—0.006	0.006	0.011	—0.011	—0.001	—0.009	0.003	0.580 (0.714)			
0.141	—0.141	0.150	—0.028	0.0	0.0	0.0	0.028	1.242 (1.088)		
—0.153	0.079	0.078	—0.081	0.068	0.0	—0.068	0.081	0.013	1.212 (1.062)	
0.0	—0.131	0.154	0.0	—0.039	0.071	—0.039	0.0	0.0	0.0	1.497 (1.312)

947 cm^{-1} should be attributed to an out-of-plane mode instead (see also ref. 22), they do not confirm his assignment (i.e., the band at 897 cm^{-1} to ν_3 (B_1)). As shown in Table 5, the band at 1227 cm^{-1} should be assigned to ν_3(B_1) and the 897 cm^{-1} band to ν_{15}(B_1). The band at 1105 cm^{-1} (previously assigned to ν_{15}) is attributed to a combination band of two out-of-plane frequencies: [ν_4 + ν_{16b}] 391 + 713 = 1104 cm^{-1}.

It is not self-evident that the 897 cm^{-1} band should be assigned to ν_{15}. The calculated value of 881 cm^{-1} does not enable a choice to be made between the bands at 867 cm^{-1} (A_2 according to WB [21]) and 897 cm^{-1} (B_2 according to WB [21]). If the band at 947 cm^{-1} corresponded to an A_2 mode [22], the band at 867 cm^{-1} should be assigned to ν_{15}. However, an A_2 fundamental of the C_{2v} point group appears only in the Raman spectrum and not in the infrared: the band at 947 cm^{-1}, however, shows no Raman activity and is assigned to a B_2 fundamental, and hence the 897 cm^{-1} band to ν_{15}.

TABLE 5

Experimental and calculated frequencies of deuterated pyridines of C_{2v} symmetry (in cm^{-1}); the originally assigned values appear in parentheses

Symmetry	Notation [19]	4-d_1		2,6-d_2		3,5-d_2		d_5		Character of vibration from the CNDO/2 force method
		obs. [20]	calc.	obs. [21]	calc.	obs. [21]	calc.	obs. [19]	calc.	
A_1	ν_1	989	978	986	971	967	972	962	958	α(CCC), (ν(CN), ν(CC))
	ν_2	3045[c] (3033)	3071	3065	3092	2297	2262	2293	2284	ν(CH)
	ν_{6a}	597	582	578	582	596	582	582	570	α(CCC), (resp. α(NCC))
	ν_{8a}	1575	1635	1586	1602	1577	1630	1530	1585	ν(CC)
	ν_{9a}	1215	1203	889	874	1179	1147	887	880	β(CH)
	ν_{12}	1010[c] (1015)	1003	1019	1005	1029	996	1006	981	α(CCC), (resp. α(NCC))
	ν_{13}	2287	2276	2260	2239	3047	3088	2270	2259	ν(CH)
	ν_{18a}	1068	1053	1087	1096	828	831	823	824	β(CH), ν(CN)
	ν_{19a}	1476	1492	1457	1444	1436	1434	1340	1353	β(CH), ν(CN)
	ν_{20a}	3012	3037	3002	3066	3000	3039	2254	2234	ν(CH)
B_1	ν_3	1215	1217	1184	1174	1227[d] (947)	1208	1043[a] (908)	1041	ν(CC), β(CH)
	ν_{6b}	648	666	635	659	642	658	625	645	α(CCC)
	ν_{7b}	3035	3038	2252	2238	3049	3039	2285	2236	ν(CH)
	ν_{8b}	1559	1585	1568	1583	1589	1585	1542	1553	ν(CN), ν(CC)
	ν_{14}	1347	1340	1243[d] (1345)	1237	1328	1347	1301[a] (1322)	1263	ν(CN), β(CH)
	ν_{15}	1086	1090	1128	1124	897[d] (1105)	881	833[b] (887)	847	β(CH)
	ν_{18b}	862	864	915[d] (860)	909	1081	1066	833	831	β(CH)
	ν_{19b}	1413	1383	1415	1423	1411	1378	1228[a] (1301)	1215	β(CH)
	ν_{20b}	3069	3072	3067	3071	2281	2265	2293	2267	ν(CH)

[a]From ref. 23. [b]From ref. 24. [c]From ref. 21. [d]Values reassigned in this paper.

TABLE 6

Calculated intensities (in cm mmol^{-1})

Symmetry ν_i	Notation [19]	Pyridine				
		d_0	4-d_1	2,6-d_2	3,5-d_2	d_5
A_1	ν_1	698	182	28	5	61
	ν_2	9603	511	6644	11063	5616
	ν_{6a}	36	29	42	24	23
	ν_{8a}	4164	3874	4761	3853	4247
	ν_{9a}	79	80	12	286	420
	ν_{12}	8	635	2	225	4
	ν_{13}	4691	3118	7276	604	2526
	ν_{18a}	451	396	395	395	74
	ν_{19a}	604	598	0	592	0
	ν_{20a}	7892	5211	2946	3096	4929
B_1	ν_3	20	57	463	252	4
	ν_{6b}	98	109	84	103	99
	ν_{7b}	64	7892	56	4181	1057
	ν_{8b}	1029	1500	980	1192	1646
	ν_{14}	570	40	52	8	229
	ν_{15}	192	144	283	0	14
	ν_{18b}	35	35	300	325	443
	ν_{19b}	1924	1848	1527	2303	1049
	ν_{20b}	6020	9597	6344	5281	3043

In the case of pyridine-d_5, the calculated frequencies support the reassignments by Zerbi et al. [23] of the $\nu_3(B_1)$, $\nu_{14}(B_1)$ and $\nu_{19b}(B_1)$ modes, and that by Suzuki and Orville-Thomas [24] of the $\nu_{15}(B_1)$ mode of the original CFL assignment [19] (Table 5).

In conclusion, the mean deviation for the 95 frequencies is 18 cm^{-1}, which proves that useful results can be obtained by employing only 5 parameters.

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